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3D Computer Models of Mo-Zr-V, Ti-C-V, Ti-Ir-Ru T-x-y Diagrams with Three-phase Reaction Type Changing

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Temperature and concentration borders of experimentally discovered effects of three-phase reactions type changing in systems Mo-Zr-V, Ti-C-V, Ti-Ir-Ru had been determined and confirmed by their T-x-y diagrams 3D computer models. Such kind effects had been found also in other three-phase regions of systems Ti-C-V and Ti-Ir-Ru.

Keywords: 3D Computer Model, Three-Phase Reaction Type Changing, Mo-Zr-V, Ti-C-V, Ti-Ir-Ru.

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1. INTRODUCTION

There are such kind of three-phase regions in T-x-y diagrams, where phase reaction type changing takes a place inside it. For instance, the peritectic reaction $L+R\rightarrow B$ carries out in one part of the region L+B+R of the system Mo-Zr-V=A-B-C (where binary compounds $ZrMo_2$ and ZrV_2 in the ternary system form a solid solution R [1]), nearer to the binary system Mo-Zr, and the eutectic reaction $L\rightarrow B+R$ fulfills in another part inside the region nearer to the binary system Zr-V (Fig. 1). Hence, transformation from one type reaction to another must be somewhere inside the region. However there are some three-phase regions, which have changing of phase reaction type too, but special methods should be used to define temperature and concentration borders.

All given in literature views about methods of phase reaction type changing definition may be divided into two groups [2]. One of them unifies different methods, based on construction of tangents to directing curves of ruled surfaces, which serve borders of a three-phase region (the tangent method). Other methods are based on decomposition of investigated alloy mass to mass portions of three coexisting phases at two different values of temperature to estimate mass portions increment signs at temperature changing. It was firstly proved in 1945 [3] that phase reaction type is changing in some temperature interval, but not at a constant temperature as in the tangent method. Later it was demonstrated [4] that if to express the decomposition of initial mass G to mass portions of three material points m_A, m_B and m_L at some temperature T as $G=Am_A+Bm_B+Lm_L$, then it is necessary to consider at $T-dT$ a total differential

$$dG = dAm_A + Adm_A + dBm_B + Bdm_B + dLm_L + Ldm_L = 0 \quad (1.1)$$

and do not use only the expression

$$dG = dAm_A + dBm_B + dLm_L + Ldm_L = 0 \quad (1.2)$$

at $dm_A=dm_B=0$, if to suppose the absence of limited

solubility of solid phases, as it takes a place in the tangent method.

The method to find at a given temperature the line, which divide tie-triangle into parts so, that the eutectic reaction $(L\rightarrow A+B)$ carries out in one part, but the peritectic reaction $(L+B\rightarrow A)$ fulfills in the other part, was proposed in the same paper [4]. This line corresponds to the state, when the three-phase reaction becomes the two-phase one $(L\rightarrow A)$ in a presence of third phase (B): $\Delta m_B=0$. For instance, the line *ab* divides into two parts the tie-triangle of the isothermal section of the system Mo-Zr-V at 1532.4oC (Fig. 2,a) - the temperature of type reaction changing of the alloy G(0.3, 0.6, 0.1) (Fig. 1,c).

If to apply the equation (1) to any three-phase region, then:

1) Its own surface corresponds to zero value of mass portion increment of every of three coexisting phases inside three-phase region in T-x-y diagram [5]. For instance, the surface *abc* (Fig. 1) inside the three-phase region L+B+R in the system Mo-Zr-V T-x-y diagram corresponds to the changing of a role of the compound R in three-phase reaction from the reagent to the product of this reaction.

2) This surface of zero increment of mass portion of one of three phases is the ruled surface and it is formed by horizontal generated line inside the three-phase region [6]. As the three-phase reaction on it is transformed to two-phase one, then the surface may be named the two-phase reaction surface.

3) Theoretically there are always all three surfaces, which correspond to zero increment of mass portion of every phase, inside any three-phase region with unlimited borders, but any of such kind surfaces can appear only in specific conditions in concrete temperature intervals, so a three-phase region in a real system can have from one to three surfaces or it can have none of them [6].

4) Tracks of these surfaces sections are in isotherms and isopleths (Fig. 2).

5) Changing of mass portion increment sign of one

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of three phases at transformation of phase reaction type from eutectic to peritectic or vice versa influences on concentration of microstructure [7].

The algorithm of two-phase reaction surface in three-phase region construction belongs to software of T-x-y diagrams 3D computer models design [8].
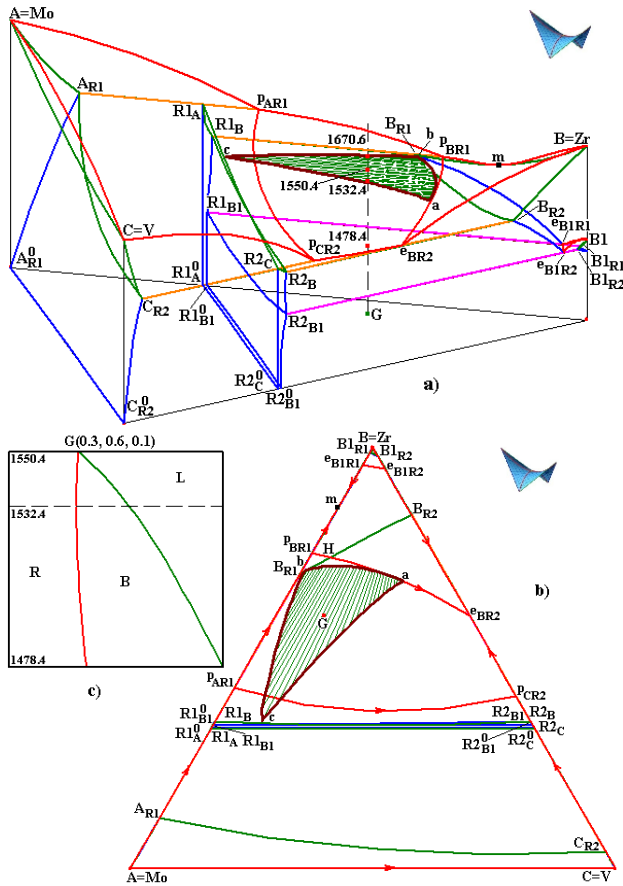

Fig. 1 – 3D computer model of the system A-B-C=Mo-Zr-V T-x-y diagram with compounds $R1=ZrMo_2=R$, $R2=ZrV_2=R$ (R1 and R2 form solid solution) (a), x-y projection (b), mass balances for the melt G(0.3, 0.6, 0.1) with transformation of peritectic reaction $L+R\rightarrow B$ to eutectic one $L\rightarrow B+R$ ($\Delta m_R=0$, $\Delta m_L<0$, $\Delta m_B>0$) at 1532.4°C (c)

2. SYSTEM Mo-Zr-V

Changing of the phase reaction type in the region L+B+R of the system Mo-Zr-V had been defined experimentally [1, p. 439-442]. The surface *abc* of two-phase reaction $L\rightarrow B$ in the presence of a passive phase R at $\Delta m_R = 0$ had been designed with a help of the 3D computer model.

It is conveniently to visualize three-phase reaction changing in so called mass balances [7, 8]. For instance, crystallization of the alloy G(0.3, 0.6, 0.1) is beginning at the temperature 1670.6°C, when the vertical line in the point G intersects the liquidus surface of the compound R (Fig. 1,a). Further it intersects upper and then lower borders of the three-phase region L+B+R, correspondingly, at temperatures 1550.4°C and 1478.4°C (Fig. 1,c). Peritectic reaction $L+R\rightarrow B$ with decreasing of liquid L and solid solution R portions ($\Delta m_L<0$, $\Delta m_R<0$) has a place in the interval 1550.4-1532.4°C. The vertical line in the point G intersects the

surface $\Delta m_R=0$ at 1532.4°C. The binary eutectic B+R is crystallizing below this temperature and the sign of the increment Δm_R is changing from minus to plus. It can see intersections of the surface $\Delta m_R=0$ as the line *ab* in the isothermal section (Fig. 2,a) and as the curve *ab* in the isopleth (Fig. 2,b).
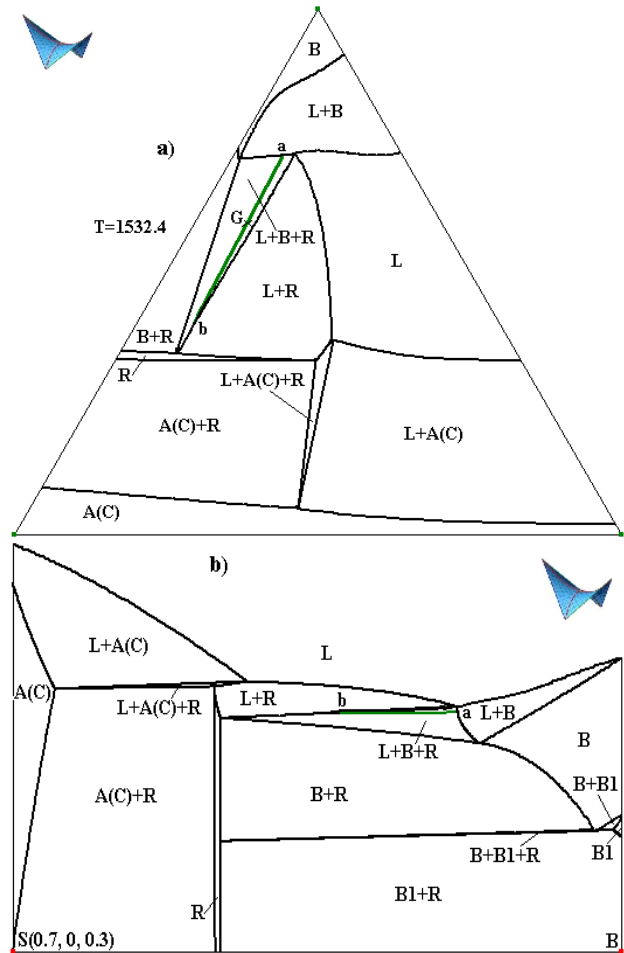

Fig. 2 – Isothermal section 1532.4°C (a) and isopleths S(0.5, 0, 0.5)-B (b) of the system Mo-Zr-V

3. SYSTEM Ti-C-V

They say [1, p. 301] about reaction type changing along the curve $p_{AR1}Q$ with minimum m at 1575°C (Fig. 3) and that "tie-line, which corresponds to this minimum, is the border between peritectic and eutectic parts of the diagram" in the system Ti-C-V. Really, temperature of this changing for different melts does not constant (1575 °C). It changes on the surface *abc* of the two-phase reaction $L\rightarrow A(C)$ at $\Delta m_{R1(R2)} = 0$ (Fig. 4).

Repeating three times changing of phase reactions from peritectoid type to eutectoid one has a place also in the region A(C)+R1(R2)+R3 with three surfaces of two-phase reactions, which intersect along the curve *ab* (Fig. 5).
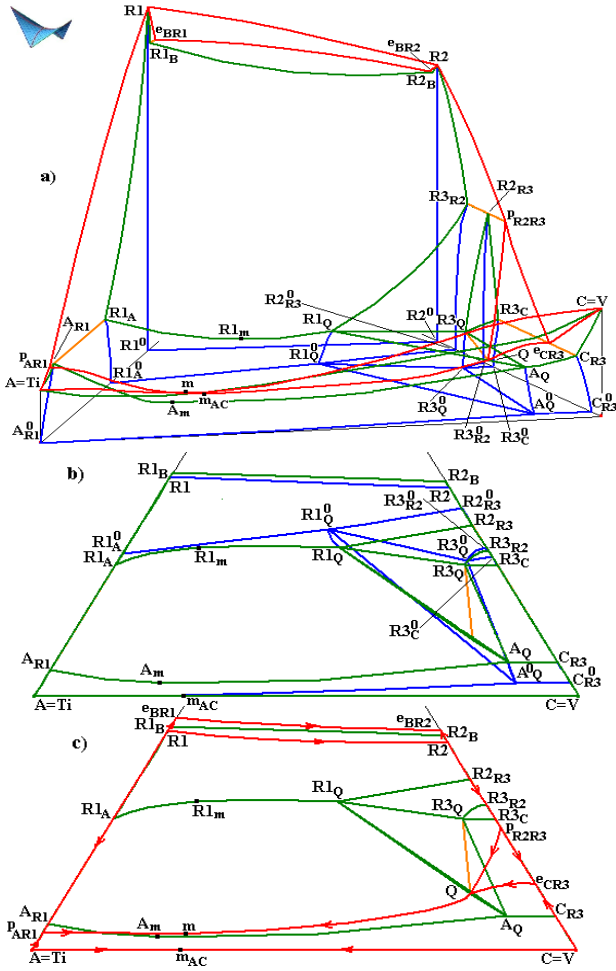
Fig. 3 – 3D computer model of the system A-B-C=Ti-C-V with compounds R1=TiC, R2=C$_{0.9}$V, which form solid solution R1(R2), and R3=CV$_2$ (a), x-y projections of solidus+solvus (b) and liquidus+solidus (c)
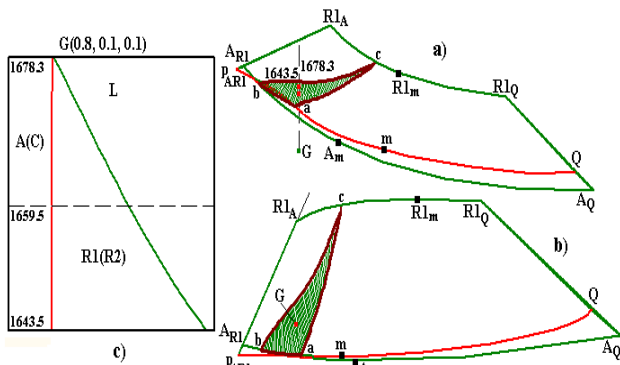

Fig. 4 – Mass balances for the melt G(0.8, 0.1, 0.1) with changing of peritectic reaction L+R1(R2)→A(C) to eutectic one L→A(C)+R1(R2) ($\Delta m_{R1(R2)}$=0, Δm_L<0, $\Delta m_{A(C)}$>0) at 1659.5°C (c) on the surfaces *abc* inside the 3-phase region L+A(C)+R1(R2), drawn in T-x-y (a) and x-y (b) projections
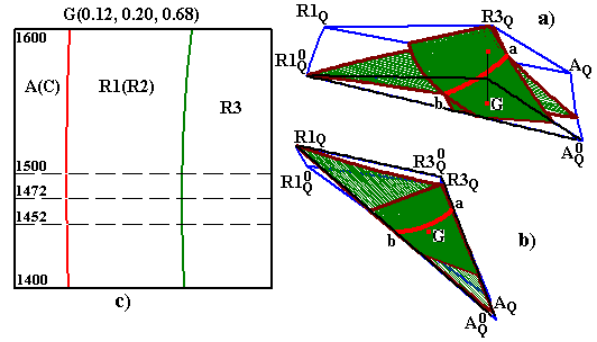

Fig. 5 – Mass balances for the melt G(0.12, 0.20, 0.68) with change of peritectoid reaction R1(R2)+A(C)→R3 to eutectoid one R1(R2)→A(C)+R3 ($\Delta m_{A(C)}$=0, $\Delta m_{R1(R2)}$<0, Δm_{R3}>0) at 1500°C with the next changing of it to peritectoid reaction R1(R2)+R3→A(C) (Δm_{R3}=0, $\Delta m_{R1(R2)}$<0, $\Delta m_{A(C)}$>0) at 1472°C and again to eutectoid one R3→A(C)+R1(R2) ($\Delta m_{R1(R2)}$=0, Δm_{R3}<0, $\Delta m_{A(C)}$>0) at 1452°C (c) inside the 3-phase region A(C)+R1(R2)+R3, drawn in T-x-y (a) and x-y (b) projections
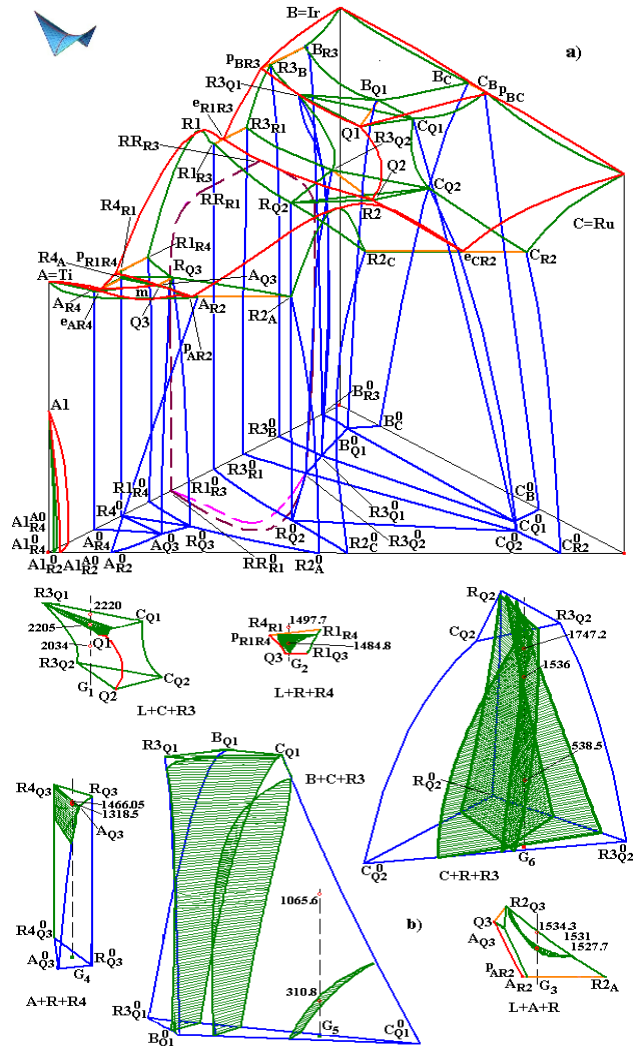

Fig. 6 – 3D computer model of the system A-B-C=Ti-Ir-Ru T-x-y diagram with binary compounds R1=TiIr=δ=R, R2=TiRu=δ=R (in the ternary system they form solid solution R), R3=TiIr$_3$=ε, R4=Ti$_3$Ir=γ (second order transformation R=R' is shown by dashed lines) (a) and 3-phase regions with 2-phase reaction surfaces (b)

4. SYSTEM Ti-Ir-Ru

Changing of eutectic reaction L→ε+Ru (or L→C+R3, ε=R3=TiIr₃) to peritectic one L+ε→Ru (or L+R3→C) in the system A-B-C=Ti-Ir-Ru had been founded from experiments [9]. 3D computer model of Ti-Ir-Ru T-x-y diagram had been designed by MSIT data [11] (Fig. 3,a). It gives opportunity to confirm the reaction type changing in the region L+C+R3 and moreover to discover this kind effects in two regions L+A+R, L+R+R4 with liquid and in three regions A+R+R4, B+C+R3, C+R+R3 in sub-solidus (Fig. 3,b) [6].

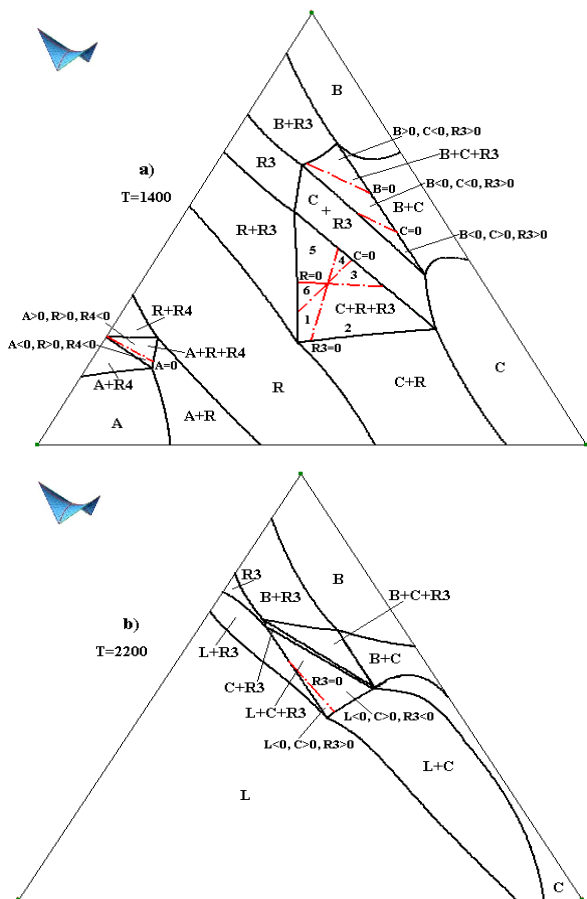**Fig. 8** – Isothermal sections T=1400°<T_{Q3} (in the region C+R+R3: 1 - C>0, R<0, R3>0, 2 - C>0, R<0, R3<0, 3 - C>0, R>0, R3<0, 4 – C<0, R>0, R3<0, 5 - C<0, R>0, R3>0, 6 - C<0, R<0, R3>0, (second-order phase transformation R=R' is not shown) (a) and T₂<T=2200°<T_{Q1} (b) of the system Ti-Ir-Ru
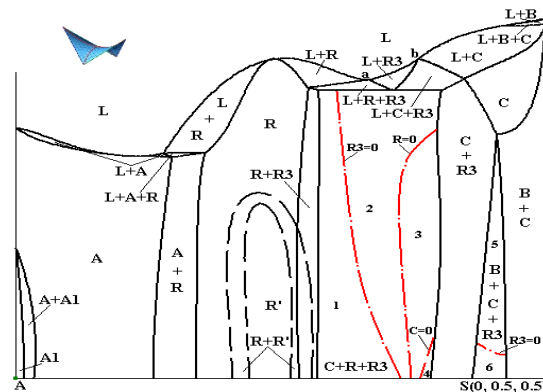

Fig. 7 – Isopleth A-S(0, 0.5, 0.5) (second-order phase transformation R=R' is shown by dashed lines; sections of surfaces for two-phase reactions are shown by dash-dotted lines; curve *ab* is present at this isopleths in (Yeremenko et al, 2011), but is absent in (MSIT), phase reactions within region C+R+R3 – 1(R→C+R3), 2(R+R3→C), 3(R3→C+R), 4(C+R3→R) & within region B+C+R3 – 5(B→C+R3), 6(B+R3→C) of the system Ti-Ir-Ru

Tracks of two-phase reaction surfaces are presented in isothermal sections and isopleths (Figures 7, 8). Dash-dotted lines show sections of these kind surfaces. They divide isothermal sections of three-phase regions into fragments with different signs of mass portions increments of coexisting phases. For instance, the isothermal section 1400°C of the region B+C+R3 has tracks of sections of two from three two-phase reaction surfaces: Δm_B=0 and Δm_C=0, and the third surface Δm_{R3}=0 is below 1400°C (Figure 8,a). The isothermal section is divided into 3 fragments: eutectoid reactions C→B+R3 (Δm_B>0, Δm_C<0, Δm_{R3}>0) and B→C+R3 (Δm_B<0, Δm_C>0, Δm_{R3}>0) carry out in upper and bottom fragments, peritectoid one B+C→R3 (Δm_B<0, Δm_C<0, Δm_{R3}>0) proceeds in the fragment between them.

5. CONCLUSIONS

Three-dimensional computer model, except visualization of projections and sections, is able to detect effects of three-phase transformations types changing, to determine their temperature borders, to design corresponding surfaces of two-phase reactions. Tracks of these kind surfaces sections are drawn in isothermal sections and isopleths.

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